

Inorganic speciation of dissolved elements in seawater: the influence of pH on concentration ratios

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Article

Assessments of inorganic elemental speciation in seawater span the past four decades. Experimentation, compilation and critical review of equilibrium data over the past forty years have, in particular, considerably improved our understanding of cation hydrolysis and the complexation of cations by carbonate ions in solution. Through experimental investigations and critical evaluation it is now known that more than forty elements have seawater speciation schemes that are strongly influenced by pH. In the present work, the speciation of the elements in seawater is summarized in a manner that highlights the significance of pH variations. For elements that have pH-dependent species concentration ratios, this work summarizes equilibrium data ($S = 35$, $t = 25$ °C) that can be used to assess regions of dominance and relative species concentrations. Concentration ratios of complex species are expressed in the form $\log[A]/[B] = \text{pH} - C$ where brackets denote species concentrations in solution, A and B are species important at higher (A) and lower (B) solution pH, and C is a constant dependent on salinity, temperature and pressure. In the case of equilibria involving complex oxy-anions ($\text{MO}_x(\text{OH})_y$) or hydroxy complexes ($\text{M}(\text{OH})_n$), C is written as $\text{p}K_n = -\log K_n$ or $\text{p}K_n^* = -\log K_n^*$ respectively, where K_n and K_n^* are equilibrium constants. For equilibria involving carbonate complexation, the constant C is written as $\text{p}Q = -\log(K_2/K_n[\text{HCO}_3^-])$ where K_2 is the HCO_3^- dissociation constant, K_n is a cation complexation constant and $[\text{HCO}_3^-]$ is approximated as 1.9×10^{-3} molar. Equilibrium data expressed in this manner clearly show dominant species transitions, ranges of dominance, and relative concentrations at any pH.

Introduction

Solution speciation exerts important controls on chemical behavior. Speciation is known to influence solubility, membrane transport and bioavailability, adsorptive phenomena and oceanic residence times, volatility, oxidation/reduction behavior, and even physical properties of solutions such as sound attenuation. In recognition of such influences, substantial efforts have been made to characterize the chemical speciation of elements in seawater. While assessments of organic speciation have dominantly been obtained using modern voltammetric procedures and, as such, have a relatively short history, assessments of inorganic speciation typically involve a wide variety of analytical procedures that have been employed over many decades.

Assessments of the inorganic speciation of seawater began with attempts¹ to determine dominant chemical forms in seawater based on available thermodynamic data. Early compilations of Principal Species² dominantly involved (a) simple hydrated cations and anions (e.g. Na^+ , Ca^{2+} , Cl^- , F^-), (b) ion pairs with sulfate (e.g. MgSO_4^0 and CaSO_4^0), (c) fully hydrolyzed elements (e.g. $\text{H}_m\text{PO}_4^{m-3}$, $\text{H}_m\text{AsO}_4^{m-3}$, MoO_4^{2-} and WO_4^{2-}) and (d) chloride complexes (e.g. AuCl_2^- , HgCl_4^{2-}). While it was noted^{1,2} that hydroxide complexes were important for all ions with oxidation numbers greater than two, hydroxide complexes were notably absent in Principal Species tabulations until the following decade.

The thermodynamic data compilations of Sillén and Martell^{3,4} catalyzed rapid advances in equilibrium models of seawater speciation. These works were followed by additional compilations⁵⁻⁷ that were critically important to modern seawater speciation assessments. In view of these developments, and additional extensive experimental analyses appropriate to seawater, Principal Species assessments ten to fifteen years after

the pioneering work of Sillén demonstrated a much improved awareness of the importance of hydrolysis in elemental speciation.⁸⁻¹⁰

An additional major speciation assessment¹¹ provided a greatly improved, comprehensive view of inorganic complexation in seawater. Based on the analogous characteristics of metal complexation by carbonate and oxalate, Turner *et al.*¹¹ concluded that rare earth element complexation in seawater is dominated by carbonate. Subsequently, as the result of approximately twenty years of progress in seawater speciation, the Principal Species assessment of Bruland¹² listed seventeen elements with carbonate-dominated Principal Species.

Speciation calculations

Based on currently available data, Principal Species for a substantial portion of the periodic table (through atomic number 103) are thought to be controlled or influenced by pH. The main objective of the present work is a review of Principal Inorganic Species for the elements in seawater. The principal focus of this work is an assessment of the influence of pH on inorganic speciation.

The Principal Species assessment in this work differs from previous presentation formats in its objective of providing a simple quantitative means of assessing Principal Species variations with changes in pH. Stepwise equilibrium constants provide a simple means of assessing species concentration ratios as a function of pH. In the case of equilibria involving simple protonation of complex anions, $\text{MO}_x(\text{OH})_y^{n-}$, stepwise equilibrium constants are expressed in the form

$$\frac{[\text{H}^+][\text{H}_m\text{A}^{m-n}]}{[\text{H}_{m+1}\text{A}^{m+1-n}]} = K_{n-m}, \quad (1)$$

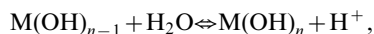
where $\text{A}^{n-} = \text{MO}_x(\text{OH})_y^{n-}$. Consequently,

$$\log \frac{[H_m A^{m-n}]}{[H_{m+1} A^{m+1-n}]} + \log[H^+] = \log K_{n-m}$$

and

$$\log[H_m A^{m-n}]/[H_{m+1} A^{m+1-n}] = -pK_{n-m} + \text{pH} \quad (2)$$

where $\text{pH} = -\log[H^+]$ and $pK_{n-m} = -\log K_{n-m}$. In the case of simple stepwise hydrolysis equilibria,



stepwise hydrolysis constants are written as

$$K_n^* = \frac{[M(\text{OH})_n][\text{H}^+]}{[M(\text{OH})_{n-1}]} \quad (3)$$

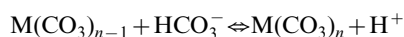
whereupon,

$$\log \frac{[M(\text{OH})_n]}{[M(\text{OH})_{n-1}]} = \log K_n^* - \log[H^+]$$

and

$$\log \frac{[M(\text{OH})_n]}{[M(\text{OH})_{n-1}]} = -pK_n^* + \text{pH} \quad (4)$$

In the case of equilibria involving carbonate, due to the near constancy of HCO_3^- concentrations in seawater, equilibria can be conveniently written in the following form



and

$$\frac{[M(\text{CO}_3)_n]}{[M(\text{CO}_3)_{n-1}]} = (K_n[\text{HCO}_3^-])(K_2'[\text{H}^+]^{-1}) \quad (5)$$

where

$$K_2' = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \text{ and } K_n = \frac{[M(\text{CO}_3)_n]}{[M(\text{CO}_3)_{n-1}][\text{CO}_3^{2-}]}$$

Using the dissociation constant of HCO_3^- in seawater (K_2'), and K_n values appropriate to various carbonate complexation equilibria in seawater, the relative concentrations of $M(\text{CO}_3)_n$ and $M(\text{CO}_3)_{n-1}$ can be written as

$$\log[M(\text{CO}_3)_n]/[M(\text{CO}_3)_{n-1}] = -pQ_n + \text{pH} \quad (6)$$

where $\log Q = \log(K_n K_2'/[\text{HCO}_3^-]) = -pQ_n$ and $[\text{HCO}_3^-]$ is assumed to be well approximated as 1.9×10^{-3} M (*i.e.* $\log[\text{HCO}_3^-] = -2.72$).

Based on equilibrium data compilations including Smith and Martell,^{5,6} Martell and Smith,⁷ Baes and Mesmer,¹³ Turner *et al.*,¹¹ Byrne *et al.*,¹⁴ and Liu and Byrne,¹⁵ Table 1 provides a compilation of pK_n , pK_n^* and pQ_n data, and equilibrium speciation schemes appropriate to seawater ($S = 35$) at 25 °C. The first two columns of Table 1 provide each element's atomic number and identity. The third column provides either (a) each element's dominant forms and speciation, or (b) the chemical species whose relative concentrations are to be evaluated using the data in column 4. As an example of the use of Table 1, the entry for Be indicates that the concentrations of Be^{2+} and BeOH^+ are equal in seawater (25 °C) at pH 5.69 and the concentrations of $\text{Be}(\text{OH})^+$ and $\text{Be}(\text{OH})_2^0$ are equal at pH 8.25. Hence, at pH 8.0 BeOH^+ is the dominant species and the ratios $[\text{Be}^{2+}]/[\text{BeOH}^+]$ and $[\text{Be}(\text{OH})_2^0]/[\text{BeOH}^+]$ are calculated as $10^{-2.31}$ and $10^{-0.25}$. The pK^* and pQ entries for Cu^{II} indicate that

$$\log([\text{CuOH}^+]/[\text{Cu}^{2+}]) = -8.11 + \text{pH}$$

and

$$\log([\text{CuCO}_3^0]/[\text{Cu}^{2+}]) = -6.93 + \text{pH}$$

As such, it is immediately seen that Cu^{2+} is a minor species relative to CuCO_3^0 in seawater (*e.g.* $[\text{CuCO}_3^0]/[\text{Cu}^{2+}] \cong 18.6$ at pH 8.2) and that the $\text{CuCO}_3^0/\text{CuOH}^+$ concentration ratio is approximately 15 ($\log 15 \cong 1.18 = 8.11 - 6.93$), independent of pH.

Discussion

Table 1 indicates that the elements in group 1 (H, Li, Na, K, Cs, Rb) exist prominently as free hydrated cations. About 1% or less of each metal is ion paired with sulfate ($[\text{MSO}_4^-]/[\text{M}^+] \sim 0.01$). Hydrogen ions are an exception to this generalization. The $\text{HSO}_4^-/\text{H}^+$ concentration ratio in seawater is approximately 0.3.

Group 2 elements (Be, Mg, Ca, Sr, Ba) are more strongly ion paired with SO_4^{2-} than most of the group 1 ions. Mg^{2+} is approximately 10% ion paired with SO_4^{2-} and the extent of SO_4^{2-} ion pairing increases somewhat for the heavier members of the group. Be^{2+} is the only member of group 2 with an ionic radius sufficiently small to induce extensive hydrolysis. The pK^* values listed for Be in Table 1 indicate that BeOH^+ is the dominant form of beryllium except at high pH. With a normal seawater pH range between approximately 7.4 and 8.35 (on the free hydrogen ion concentration scale) the $\text{Be}(\text{OH})^+/\text{Be}^{2+}$ concentration ratio is never smaller than fifty.

The pK^* and pQ compilations in Table 1 demonstrate that all group 3 elements (Sc, Y and La through Lu) are strongly complexed in seawater. Sc is the only group 3 metal that is strongly hydrolyzed. At pH 8.0 (*i.e.*, 1.6 pH units above the Sc pK_3^* and 1.6 units below pK_4^*) the dominant form of Sc^{III} is $\text{Sc}(\text{OH})_3^0$ and the $\text{Sc}(\text{OH})_3^0/\text{Sc}(\text{OH})_2^+$ and $\text{Sc}(\text{OH})_3^0/\text{Sc}(\text{OH})_4^-$ concentration ratios are both equal to approximately 40. Yttrium and the rare earth elements (Y and La–Lu) are dominantly complexed by carbonate. The pQ_n values for these elements shown in Table 1, calculated using the results of Liu and Byrne,¹⁵ indicate that MCO_3^+ is generally the dominant form for the lighter elements while $\text{M}(\text{CO}_3)_2^-$ is dominant for the heavier elements. LaCO_3^+ is the dominant form of La even at the highest pH of seawater ($\text{pH} \cong 8.35$, $pQ_2 = 8.47$) and $\text{Lu}(\text{CO}_3)_2^-$ is the dominant form of Lu if $\text{pH} > pQ_2 = 7.42$.

Group 4 elements (Ti, Zr, Hf) are all strongly hydrolyzed. $\text{Ti}(\text{OH})_4^0$ is the dominant form of Ti over a wide range of pH ($\text{pH} > 2.5$). The speciation characteristics of Zr and Hf are very similar. $\text{Zr}(\text{OH})_5^-$ is the dominant form of Zr^{IV} above pH 5.99 and $\text{Hf}(\text{OH})_5^-$ is the dominant form of Hf^{IV} above pH 6.19. Thus, for both Zr^{IV} and Hf^{IV} , the uncharged species, $\text{M}(\text{OH})_4^0$ is a significant but minor species. At the lowest pH of seawater the $\text{Zr}(\text{OH})_4^0/\text{Zr}(\text{OH})_5^-$ and $\text{Hf}(\text{OH})_4^0/\text{Hf}(\text{OH})_5^-$ concentration ratios are approximately 0.04 and 0.06 respectively.

Group 5 elements (V, Nb, Ta) are strongly hydrolyzed. With the smallest ionic radius of these three elements, V^{V} is very strongly hydrolyzed. $\text{VO}_3(\text{OH})^{2-}$ is the dominant form of V^{V} above pH 7.4. Since the pK_3 value for $\text{VO}_3(\text{OH})^{2-}/\text{VO}_4^{3-}$ is nearly two units higher than that for $\text{HPO}_4^{2-}/\text{PO}_4^{3-}$ at zero ionic strength, only $\text{VO}_2(\text{OH})_2^-$ and $\text{VO}_3(\text{OH})^{2-}$ appear to be relatively abundant within the normal pH range of seawater. $\text{Nb}(\text{OH})_6^-$ is the dominant form of Nb^{V} above pH 7.4, and since the $\text{Nb}(\text{OH})_4^+/\text{Nb}(\text{OH})_5^0$ concentration ratio in seawater is smaller than 10^{-8} only $\text{Nb}(\text{OH})_5^0$ and $\text{Nb}(\text{OH})_6^-$ are significant species in seawater. $\text{Ta}(\text{OH})_5^0$ is the dominant form of Ta^{V} in seawater. The $\text{Ta}(\text{OH})_6^-/\text{Ta}(\text{OH})_5^0$ concentration ratio is only on the order of 0.06 at the highest pH of seawater and, as is the case for Nb, cationic species are unimportant ($\text{Ta}(\text{OH})_4^+/\text{Ta}(\text{OH})_5^0 < 10^{-8}$). Thus, dominant forms for the group 5 elements are $\text{VO}_3(\text{OH})^{2-}$, $\text{Nb}(\text{OH})_6^-$ and $\text{Ta}(\text{OH})_5^0$.

Group 6 elements (Cr, Mo, W) are all strongly hydrolyzed.

Table 1 A compilation of pK_n , pK_n^* , pQ_n data and equilibrium speciation schemes appropriate to seawater ($S = 35$) at 25 °C. Equilibrium constants are expressed on the free hydrogen ion concentration scale

Atomic number	Element	Principal species	Equilibrium data
1	H	H^+ (68%), HSO_4^- (29%), HF^0 (3%)	
2	He	He	
3	Li	Li^+ (98%), $LiSO_4^-$ (2%)	
4	Be	$Be^{2+}/BeOH^+/Be(OH)_2^0$	$pK_1^* = 5.69$; $pK_2^* = 8.25$
5	B	$B(OH)_3^0/B(OH)_4^-$	$pK^* = 8.74$
6	C	$CO_2/HCO_3^-/CO_3^{2-}$	$pK_1 = 6.00$; $pK_2 = 9.09$
7	N	NO_3^- , NO_2^- , N_2 , NH_4^+/NH_3	$pK = 9.35$
8	O	O_2	
9	F	F^- (50%), MgF^+ (50%)	
10	Ne	Ne	
11	Na	Na^+ 98%, $NaSO_4^-$ (2%)	
12	Mg	Mg^{2+} (90%), $MgSO_4^0$ (10%)	
13	Al	$Al(OH)_2^+/Al(OH)_3^0/Al(OH)_4^-$	$pK_3^* = 5.7$; $pK_4^* = 7.7$
14	Si	$Si(OH)_4/SiO(OH)_3^-$	$pK = 9.32$
15	P	$H_2PO_4^-/HPO_4^{2-}/PO_4^{3-}$	$pK_2 = 6.10$; $pK_3 = 8.93$
16	S	SO_4^{2-} (33%), $NaSO_4^-$ (35%), $MgSO_4^0$ (20%) HSO_4^-/SO_4^{2-}	$pK \cong 1$
17	Cl	Cl^- (100%)	
18	Ar	Ar	
19	K	K^+ (99%)	
20	Ca	Ca^{2+} (89%), $CaSO_4^0$ (11%)	
21	Sc	$Sc(OH)_2^+/Sc(OH)_3^0/Sc(OH)_4^-$	$pK_3^* = 6.4$; $pK_4^* = 9.6$
22	Ti	$Ti(OH)_3^+/Ti(OH)_4^0$	$pK^* = 2.5$
23	V	$VO_2(OH)_2^-/VO_3(OH)_2^-/VO_4^{3-}$	$pK_2 = 7.4$; $pK_3 \leq 13$
24	Cr	$Cr(OH)_2^+$, $Cr(OH)_3^0$, $Cr(OH)_4^-$	$pK_3^* = 8.3$; $pK_4^* = 9.1$
25	Mn	Mn^{2+} (72%), $MnCl^+$ (21%)	
26	Fe	$Fe(OH)_2^+/Fe(OH)_3^0$, $Fe(OH)_4^-$	$pK_3^* = 6.60$; $pK_4^* = 8.5$
27	Co	Co^{2+} (65%), $CoCl^+$ (14%)	
28	Ni	Ni^{2+} (53%), $NiCl^+$ (9%)	
29	Cu	$Cu^{2+}/CuOH^+$, $Cu^{2+}/CuCO_3^0$	$pK_1^* = 8.11$; $pQ_1 = 6.93$
30	Zn	Zn^{2+} (64%), $ZnCl^+$ (16%)	
31	Ga	$Ga(OH)_2^+/Ga(OH)_3^0/Ga(OH)_4^-$	$pK_3^* = 4.4$; $pK_4^* = 6.0$
32	Ge	$Ge(OH)_4^0/GeO(OH)_3^-/GeO_2(OH)_2^{2-}$	$pK_1 = 8.98$; $pK_2 = 11.8$
33	As	$H_2AsO_4^-/HAsO_4^{2-}/AsO_4^{3-}$ $As(OH)_3/As(OH)_4^-$	$pK_2 = 6.15$; $pK_3 = 9.84$ $pK^* = 9.03$
34	Se	SeO_4^{2-} (100%) $H_2SeO_3/HSeO_3^-/SeO_3^{2-}$	$pK_1 = 2.3$; $pK_2 \leq 7.8$
35	Br	Br^- (100%)	
36	Kr	Kr	
37	Rb	Rb^+ (99%), $RbSO_4^-$ (1%)	
38	Sr	Sr^{2+} (86%), $SrSO_4^0$ (14%)	
39	Y	$Y^{3+}/YCO_3^+/Y(CO_3)_2^-$	$pQ_1 = 6.63$; $pQ_2 = 7.89$
40	Zr	$Zr(OH)_3^+/Zr(OH)_4^0/Zr(OH)_5^-$	$pK_4^* = 4.6$; $pK_5^* = 5.99$
41	Nb	$Nb(OH)_4^+/Nb(OH)_5^0/Nb(OH)_6^-$	$pK_5^* \cong -0.6$; $pK_6^* = 7.4$
42	Mo	$HMoO_4^-/MoO_4^{2-}$	$pK \cong 3.5$
43	Tc	TcO_4^- (100%)	
44	Ru	$Ru(OH)_n^{4-n}$	pK_n (?)
45	Rh	$RhCl_a(OH)_b^{3-(a+b)}$	pK_n (?)
46	Pd	$PdCl_4^{2-}/PdCl_3OH^{2-}$	$pK^* = 8.7$
47	Ag	$AgCl_3^{2-}$ (66%), $AgCl_2^-$ (26%)	
48	Cd	$CdCl^+$ (36%), $CdCl_2^0$ (45%), $CdCl_3^-$ (16%)	
49	In	$In(OH)_2^+/In(OH)_3^0/In(OH)_4^-$	$pK_3^* = 4.58$; $pK_4^* = 9.37$
50	Sn	$Sn(OH)_3^+/Sn(OH)_4^0$	$pK^* \cong 1.2$
51	Sb	$Sb(OH)_3^0/Sb(OH)_6^-$	$pK^* = 2.5$
52	Te	$Te(OH)_6^0/TeO(OH)_5^-/TeO_2(OH)_4^{2-}$ $Te(OH)_4^0/TeO(OH)_3^-/TeO_2(OH)_2^{2-}$	$pK_1 = 7.35$; $pK_2 \cong 10.2$ $pK_1 \cong 3.5$; $pK_2 = 8.85$
53	I	IO_3^- (89%); I^- (100%)	
54	Xe	Xe	
55	Cs	Cs^+ (99%)	
56	Ba	Ba^{2+} (86%), $BaSO_4$ (14%)	
57	La	$La^{3+}/LaCO_3^+/La(CO_3)_2^-$	$pQ_1 = 7.38$; $pQ_2 = 8.47$
58	Ce	$Ce^{3+}/CeCO_3^+/Ce(CO_3)_2^-$	$pQ_1 = 7.05$; $pQ_2 = 8.34$
59	Pr	$Pr^{3+}/PrCO_3^+/Pr(CO_3)_2^-$	$pQ_1 = 6.88$; $pQ_2 = 8.20$
60	Nd	$Nd^{3+}/NdCO_3^+/Nd(CO_3)_2^-$	$pQ_1 = 6.83$; $pQ_2 = 8.15$
61	Pm	$Pm^{3+}/PmCO_3^+/Pm(CO_3)_2^-$	—
62	Sm	$Sm^{3+}/SmCO_3^+/Sm(CO_3)_2^-$	$pQ_1 = 6.65$; $pQ_2 = 7.97$
63	Eu	$Eu^{3+}/EuCO_3^+/Eu(CO_3)_2^-$	$pQ_1 = 6.63$; $pQ_2 = 7.89$
64	Gd	$Gd^{3+}/GdCO_3^+/Gd(CO_3)_2^-$	$pQ_1 = 6.72$; $pQ_2 = 7.95$
65	Tb	$Tb^{3+}/TbCO_3^+/Tb(CO_3)_2^-$	$pQ_1 = 6.65$; $pQ_2 = 7.72$
66	Dy	$Dy^{3+}/DyCO_3^+/Dy(CO_3)_2^-$	$pQ_1 = 6.55$; $pQ_2 = 7.69$
67	Ho	$Ho^{3+}/HoCO_3^+/Ho(CO_3)_2^-$	$pQ_1 = 6.56$; $pQ_2 = 7.59$
68	Er	$Er^{3+}/ErCO_3^+/Er(CO_3)_2^-$	$pQ_1 = 6.50$; $pQ_2 = 7.53$
69	Tm	$Tm^{3+}/TmCO_3^+/Tm(CO_3)_2^-$	$pQ_1 = 6.43$; $pQ_2 = 7.45$
70	Yb	$Yb^{3+}/YbCO_3^+/Yb(CO_3)_2^-$	$pQ_1 = 6.30$; $pQ_2 = 7.55$
71	Lu	$Lu^{3+}/LuCO_3^+/Lu(CO_3)_2^-$	$pQ_1 = 6.36$; $pQ_2 = 7.42$
72	Hf	$Hf(OH)_3^+/Hf(OH)_4^0/Hf(OH)_5^-$	$pK_4^* = 4.7$; $pK_5^* = 6.19$

Table 1 A compilation of pK_n , pK_n^* , pQ_n data and equilibrium speciation schemes appropriate to seawater ($S = 35$) at 25 °C. Equilibrium constants are expressed on the free hydrogen ion concentration scale (*Continued*)

Atomic number	Element	Principal species	Equilibrium data
73	Ta	$\text{Ta}(\text{OH})_4^+/\text{Ta}(\text{OH})_5^0/\text{Ta}(\text{OH})_6^-$	$pK_5^* \cong -1$; $pK_6^* = 9.6$
74	W	$\text{HWO}_4^-/\text{WO}_4^{2-}$	$pK \leq 3.5$
75	Re	ReO_4^- (100%)	
76	Os	OsO_4^0 (?)	
77	Ir	$\text{IrCl}_a(\text{OH})_b^{3-(a+b)}$	pK (?)
78	Pt	$\text{PtCl}_4^{2-}/\text{PtCl}_3\text{OH}^{2-}$	$pK^* \cong 8.7$
79	Au	AuCl_2^- $\text{AuCl}_3(\text{OH})^-/\text{AuCl}_2(\text{OH})_2^-/\text{AuCl}(\text{OH})_3^-$	$pK_{22}^* = 6.4$; $pK_{13}^* = 7.4$ (?)
80	Hg	HgCl_4^{2-} (88%), HgCl_3^- (12%)	
81	Tl	Tl^+ (61%), TlCl^0 37% $\text{TlCl}_4^-/\text{Tl}(\text{OH})_3^0$	$pK \cong 7.1$ (?)
82	Pb	$\text{PbCl}_n^{2-n}/\text{PbCO}_3^0$	$pQ = 7.85$
83	Bi	$\text{Bi}(\text{OH})_2^+/\text{Bi}(\text{OH})_3^0/\text{Bi}(\text{OH})_4^-$	$pK_3^* = 4.86$; $pK_4^* \cong 12.7$

Mo and W exist solely in the VI state, while Cr is found in seawater with oxidation numbers VI and III. Mo and W have dominant species transitions near pH 3.5 ($pK_2 = 3.5$), while the $\text{HCrO}_4^-/\text{CrO}_4^{2-}$ transition for Cr^{VI} occurs near pH 5.7. As such, in the VI state, all three elements dominantly exist as MO_4^{2-} and ion pairs with Mg^{2+} , Ca^{2+} , etc. Cr^{III} is strongly hydrolyzed and, with a pK_3^* value near 8.3, $\text{Cr}(\text{OH})_2^+$ is more abundant than $\text{Cr}(\text{OH})_3^0$ except at high pH.

Group 7 elements (Mn, Tc, Re) have dissimilar group chemistries due to differences in favored oxidation numbers. Tc^{VII} and Re^{VII} exist in solution solely as TcO_4^- and ReO_4^- and should be exceptionally unreactive. Mn has two favored oxidation states with highly dissimilar characteristics. Mn^{II} exists in seawater dominantly as free hydrated ions (Mn^{2+}) and ion pairs with Cl^- . In the IV oxidation state Mn, as $\text{MnO}_2(\text{s})$, is highly insoluble. Thus, oxidation state transformations strongly influence Mn behavior in seawater.

Elements in group 8 (Fe, Ru, Os) have diverse and generally poorly understood seawater chemistries. Fe exists in seawater dominantly as Fe^{III} and, to a lesser extent, as Fe^{II}. Iron in the II oxidation number has a solution chemistry very similar to those of other M^{II} ions in period 4. Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, and Zn^{II} are all weakly ion paired with Cl^- and are present in seawater dominantly as free hydrated ions. As Fe^{III}, iron is strongly hydrolyzed. Table 1 indicates that the dominant form of Fe^{III} throughout the normal pH range of seawater is $\text{Fe}(\text{OH})_3^0$. This conclusion is somewhat controversial because (a) iron biogeochemistry is important and intensively investigated, and (b) only one somewhat problematic analytical procedure (solubility analysis) has been extensively used to investigate the $\text{Fe}(\text{OH})_2^+/\text{Fe}(\text{OH})_3^0$ and $\text{Fe}(\text{OH})_3^0/\text{Fe}(\text{OH})_4^-$ transitions. The characteristics of Ru and Os speciation in seawater are very poorly understood. It is probable that both elements are very strongly hydrolyzed. Based on available data, Principal Species for Ru and Os are tentatively assigned as $\text{Ru}(\text{OH})_n^{4-n}$ and OsO_4^0 .

Elements in group 9 (Co, Rh, Ir) have generally complex chemistries and are, perhaps, only slightly better understood than the group 8 elements. The dominant oxidation number for Co in seawater is II. Co^{II} exists predominantly as Co^{2+} and ion pairs with Cl^- . Rh^{III} is strongly complexed by chloride and is also strongly hydrolyzed. Investigations in 0.5 M NaCl (Miller and Byrne, in progress) indicate that Rh^{III} forms a complex array of mixed ligand complexes ($\text{RhCl}_a(\text{OH})_b^{3-(a+b)}$). These investigations are challenging due to slow ligand exchange kinetics. Ir^{III} forms strong chloride complexes and, as in the case of Rh^{III}, has slow ligand exchange rates. In analogy with Rh^{III} the Principal Species of Ir^{III} are tentatively assigned as $\text{IrCl}_a(\text{OH})_b^{3-(a+b)}$. Both Rh and Ir occur in the IV oxidation state but the solution chemistries of Rh^{IV} and Ir^{IV} are very poorly understood.

Group 10 elements (Ni, Pd, Pt) principally occur with

oxidation number II. Ni in seawater dominantly exists as free hydrated Ni^{2+} . The chemistries of Pd^{II} and Pt^{II} are similar and contrast sharply with the speciation of Ni^{II}. Pd and Pt exist dominantly as PdCl_4^{2-} and PtCl_4^{2-} in seawater¹⁶ but are, nonetheless, significantly hydrolyzed as $\text{PdCl}_3\text{OH}^{2-}$ and $\text{PtCl}_3\text{OH}^{2-}$ at high pH. The potential importance of Pt^{IV} species in seawater is poorly understood.

The solution chemistries of group 11 elements (Cu, Ag, Au) in oxidation state I are similar. Cu^I, Ag^I and Au^I are strongly complexed with Cl^- and hydrolysis is insignificant. While Ag solely exists as Ag^I, Cu occurs dominantly as Cu^{II} in oxygenated seawater and oxidation number III may be important for Au. Cu^{II} chemistry is dominated by carbonate complexation, while Au^{III} speciation in seawater appears (tentatively) to be dominated by mixed-ligand chlorohydroxy complexes.

The speciation of group 12 metals (Zn, Cd, Hg), all in the II oxidation state, involves a progression from very weak to very strong complexation. Zn^{II} occurs in seawater principally as Zn^{2+} and ZnCl^+ , Cd^{II} is moderately complexed (CdCl^+ , CdCl_2^0 and CdCl_3^-) and Hg^{II} is complexed very strongly as HgCl_4^{2-} and HgCl_3^- .

Group 13 elements (B, Al, Ga, In, Tl) in oxidation state III are very strongly hydrolyzed. The Principal Species of these elements are $\text{B}(\text{OH})_3^0$, $\text{Al}(\text{OH})_4^-$, $\text{Ga}(\text{OH})_4^-$, $\text{In}(\text{OH})_3^0$ and, tentatively, $\text{Tl}(\text{OH})_3^0$. The speciation of each of these elements is significantly pH dependent. For B, Al, Ga and In, each metal is partitioned between uncharged and anionic forms. In contrast, Tl^{III} appears to be partitioned between $\text{Tl}(\text{OH})_3^0$ and either TlCl_4^- or mixed chlorohydroxy species. Tl is unique among the group 13 metals in having a significant, and perhaps dominant, I oxidation state. In this form Tl^I occurs principally as the free hydrated Tl^+ ion.

Group 14 elements (C, Si, Ge, Sn, Pb) have diverse speciation characteristics. C is partitioned dominantly between CO_3^{2-} and HCO_3^- , while for both Si and Ge, uncharged forms are dominant ($\text{Si}(\text{OH})_4^0$ and $\text{Ge}(\text{OH})_4^0$) with lesser concentrations ($\leq 15\%$) of $\text{SiO}(\text{OH})_3^-$ and $\text{GeO}(\text{OH})_3^-$. The sparse data available for assessment of Sn^{IV} speciation indicate that $\text{Sn}(\text{OH})_4^0$ is dominant over a wide range of pH. The speciation of Pb is apparently unique among seawater constituents in that Pb^{II} is partitioned between chloride complexes and carbonate complexes.¹⁷ The latter are dominant above pH 7.85.

Group 15 elements (N, P, As, Sb, Bi) in oxidation states V and III are strongly hydrolyzed in seawater, and oxidation number V is favored relative to III for all group 15 elements except Bi. Bi is present in seawater dominantly as $\text{Bi}(\text{OH})_4^0$. N^V and N^{III} exist solely as unprotonated NO_3^- and NO_2^- . The $\text{NH}_4^+/\text{NH}_3^0$ ratio in seawater is significantly pH dependent and is always larger than ~ 10 . The dominant forms of P^V and As^V in seawater are HPO_4^{2-} and HAsO_4^{2-} . While $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ and $\text{H}_2\text{AsO}_4^-/\text{HAsO}_4^{2-}$ ratios are similar in seawater, the $\text{PO}_4^{3-}/\text{HPO}_4^{2-}$ ratio is substantially larger than that for

$\text{AsO}_4^{3-}/\text{HAsO}_4^{2-}$. Sb^{V} in seawater is present dominantly as $\text{Sb}(\text{OH})_6^-$. The speciation of Sb^{III} is similar to that of Bi^{III} in that $\text{Sb}(\text{OH})_3^0$ is dominant over a wide range of pH. The $\text{As}(\text{OH})_3^0/\text{As}(\text{OH})_4^-$ ratio in seawater is pH dependent and generally larger than six.

Group 16 elements include O, S, Se, Te and Po. O^{2-} and OH^- are found in association with elements in every group of the periodic table except 1, 2 and 18. Dissolved O_2 is very important in seawater because of its strong influence on the oxidation/reduction behavior of solutions. The dominant form of OH^- in seawater is MgOH^+ . S exists in oxygenated seawater as SO_4^{2-} and ion pairs with group 1 and group 2 elements, and is not significantly protonated except at very low pH. Se exists in seawater as both Se^{VI} and Se^{IV} . In the higher oxidation state Se exists as SeO_4^{2-} with protonation characteristics very similar to SO_4^{2-} ($\text{pK} \sim 1$). As Se^{IV} , selenium is partitioned between HSeO_3^- and SeO_3^{2-} with the former dominant at low pH and the latter dominant at high seawater pH. Te also exists in seawater in the VI and IV oxidation states. In the case of Te^{VI} , since $\text{pK} \approx 7.35$ for the $\text{Te}(\text{OH})_6^0/\text{TeO}(\text{OH})_5^-$ transition, $\text{TeO}(\text{OH})_5^-$ is the predominant species. For Te^{IV} , $\text{pK} \approx 8.85$ for the $\text{TeO}(\text{OH})_3^-/\text{TeO}_2(\text{OH})_2^{2-}$ partition and $\text{TeO}(\text{OH})_3^-$ is thereby predominant. Little is known about Po equilibria in solution.

The group 17 elements (F, Cl, Br, I and At) exist with $-I$ and V oxidation numbers and the $-I$ state is predominant for the lighter elements. F^- occurs in seawater as an approximately equimolar mixture of F^- and MgF^+ . Cl and Br occur dominantly as unassociated Cl^- and Br^- . The predominant oxidation number of I is V . I^{V} occurs as IO_3^- and is, to a small extent, ion paired with Mg^{2+} . I is found in seawater at substantially lower concentrations than IO_3^- . Little is known about the solution chemistry of highly radioactive At.

Overview of speciation in seawater

The results shown in Table 1 indicate that only a relatively small number of elements have major species that do not involve hydrolyzed forms or carbonate complexation. Such elements typically have oxidation numbers I, II and $-I$ and are found in groups 1, 2, 11, 12 and 17, and in period 4 (groups 7-10). Only eight to nine elements have speciation schemes that strongly involve chloride complexation. Such elements are found in groups 9 (Rh^{III} and Ir^{III}), 10 (Pd^{II} and Pt^{II}), 11 (Cu^{I} , Ag^{I} , Au^{I}), 12 (Cd^{II} , Hg^{II}) and 14 (Pb^{II}). However, of these elements both Rh and Ir are importantly influenced by hydrolysis, Pd^{II} and Pt^{II} are significantly influenced by hydrolysis, and Pb^{II} is strongly influenced by carbonate complexation. Of the very large number of hydrolyzed elemental forms in seawater, approximately 17 have speciation schemes that are strongly pH dependent. These elements include Be^{II} , Sc^{III} (groups 2 and 3), V^{V} , Nb^{V} and Ta^{V} (group 5), Cr^{III} (group 6), Fe^{III} and Ru^{III} (group 8), Rh^{III} and Ir^{III} (group 9), Bi^{III} , Al^{III} , In^{III} , Tl^{III} (group 13), C^{IV} , Si^{IV} and Ge^{IV} (group 14), P^{V} and As^{V} (group 15), Se^{IV} and Te^{IV} (group 16). As such, no elements with oxidation numbers 1, 2 and 6 (other than Be^{II}) have hydrolyzed forms whose relative concentrations are strongly pH dependent within the normal pH range of seawater. Approximately 17 elements with atomic numbers less than 92 (Cu, Pb, Y, and the lanthanides) have speciation schemes that strongly involve or are dominated by carbonate complexation. With the inclusion of U^{VI} and the 9 actinides with oxidation number III (Am-Lr), it is seen that carbonate complexation is important for a large portion of the periodic table. Altogether, including elements strongly complexed by carbonate and seventeen or more elements with pH dependent, hydrolyzed major species, it is seen that the seawater speciation of more than forty elements is strongly influenced by pH.

Elements having exceptionally poorly understood speciation

schemes in seawater include Ru and Os (group 8), Rh and Ir (group 9), Pt (group 10) and Au (group 11). Speciation of the latter four elements may be dominated by a complex array of chlorohydroxy complexes and, perhaps, a variety of types of halides. It should also be anticipated that, for metals forming strong covalently bonded species, complexation by ligands containing reduced sulfur may dramatically change future Principal Species assessments. This concern is particularly relevant to Rh, Ir, Pd, Pt, Au, Hg, and Tl.

Appreciation of the role of carbonate in seawater complexation has grown steadily over the past forty years. Experimental difficulties have impeded the progress of investigations involving the complexation of strongly hydrolyzed metals by carbonate ions. Using new technologies, however, future improvements in carbonate complexation assessments are probable and the perceived role of carbonate in trace element complexation may significantly expand.

In view of the importance of pH dependent speciation schemes for a wide variety of elements in seawater, it is important to note that substantial uncertainties remain in the equilibrium characterizations presented in Table 1. In many cases, estimated speciation schemes must be based on data obtained using a single analytical technique. It is, furthermore, particularly problematic when speciation characterizations of strongly hydrolyzed metals at high pH are based solely on solubility analyses. Among other complicating factors, the experimental solutions used in solubility analyses generally have much higher metal concentrations than are observed in the open ocean. Consequently, solubility analyses are conducive to the formation of a more complex set of hydrolyzed species (e.g., polymers and colloids) than are generally found in the oceans. Deconvolution of the data generated in such analyses can be challenging.

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